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TITLE CRYSTAL GROWTH FROM THE VAPOR IN LOW GRAVITY ENVIRONMENTS

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I. The Influence of Gravity on Crystal Growth from the Vapor

An experiment performed beyond the limits of the biosphere, be it in low earth orbit (LEO), geosynchronous orbit (GEO), or even on the lunar surface, offers the prospect of conditions, both favorable and unfavorable, which are unable to be sustained for any appreciable time on earth. Many of the desirable effects of the space environment are the result of two conditions--high vacuum and low gravitational field, otherwise referred to as microgravity. The former condition is useful for containerless processing, for one. The latter aspect of space offers a new dimension in process control for systems where gaseous or liquid phases play important roles.

The question to be posed is not what effect does microgravity have on a given process, but rather, what effect does the earth's gravity exert upon a process? The answer, in the cases of fluids and gases, is convective flow exhibited by these media. In every situation on earth where a fluid medium is subjected to a nonvertical thermal gradient, convection exists. Temperature differences give rise to density gradients, since gases expand when heated. In the presence of a gravitational field, the less dense volume of gas will be displaced by a denser, cooler volume resulting in the circulation of gases, better known as convective flow.

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Another type of convection occurs when a denser gas is above a less dense gas, corresponding to a situation where a system is heated from below. This unstable condition can be maintained if viscous forces of the medium outweigh the buoyant forces which drive the flow, allowing a given volume to equilibrate with its environment. If, on the other hand, buoyancy is greater than viscosity, the volume element rises too quickly and spontaneous flow in the form of cells or vortex rolls results. This unstable form of convection generally causes more mixing than normal convective flow.

Concentration gradients within a medium may also give rise to convective flow. Depletion of a given component within a volume element due to reaction produces a density gradient and hence buoyancy forces. Such an effect may have a significant influence upon crystal growth from the vapor.

In mathematical terms, convective flow is characterized by the ratio of buoyancy to viscous forces, or Grashof number, Gr, which is given by the expression

$$Gr = \frac{gl^3\beta\Delta T}{\mu^2} \quad , \quad (1)$$

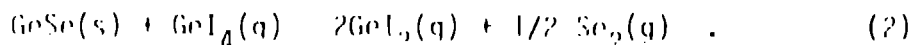
where β is the coefficient of expansion, g the acceleration of gravity, l the characteristic dimension, ΔT the temperature gradient, and μ the fluid kinematic viscosity. The actual flow velocity is given by $\sqrt{Gr\mu/l}$. Examination of Eq. (1) reveals that altering parameters other than the gravitational vector would change the value of Gr. Indeed, attempts have been made in the field of crystal growth to do so by altering reactor geometry and minimizing temperature gradient. Unfortunately, practical limits to these changes do exist. Radial thermal gradients caused by wall effects cannot be totally eliminated. As a result, some residual flows will occur. The possibility of

altering the value of G_r by substituting a value of $10^{-6}g$, the gravitational field experienced by objects in LEO, for 1 g, is readily clear. It was, and still is, the prospect of eliminating convective flow in the growth of crystals and the subsequent effects upon morphology, growth rates, and crystal homogeneity that drives the study of this process in space.

II. Crystal Growth from the Vapor-Space Experiments

Crystal growth in microgravity has been studied since the first Skylab mission. Different techniques have been employed, including growth from the melt, from solution, and from the vapor. Various materials, ranging from silicon to organic compounds, have been used. The present work deals with crystal growth from the vapor. In the past, this has been accomplished in space using the experimental technique known as chemical vapor transport (CVT). The principles behind CVT and results obtained by this method in space will be discussed here.

Chemical vapor transport was first developed by Schäfer, and the theory behind this phenomena was later refined by Kaldis, Faktor, and Garrett. In the CVT process, a solid source material reacts with a gaseous transport agent to yield only vapor phase products. The transport of GeSe(s) using GeI_4 as a transport agent serves as an example of the CVT process:



The number of gaseous species actually formed in Eq. (2) depends upon the particular chemical system. The CVT reaction takes place in a closed reaction vessel, which in zero-g studies has historically been a fused silica ampule, and the system is subjected to a temperature gradient. A schematic of this system is shown in Fig. 1. The temperature gradient causes the equilibrium constant for Eq. (2) to vary along the length of the ampule, resulting in the

establishment of concentration gradients for the different vapor species. The vapor species then migrate from the 'source' region of the vessel, where Eq. (2) favors the vapor products, to the condensation region, where the reverse reaction takes place, depositing the original solid in well-defined, single crystalline form.

In selecting experimental parameters which will optimize both crystal growth rate and morphological quality, the thermodynamics of the transport system and the mode of migration of vapor species from source to condensation region are important considerations. The former consideration will dictate the direction in which concentration gradients arise and the migration of vapor species proceeds, that is, from high to low temperature or vice versa. This aspect is critical in the selection of transport agent and temperature gradient to be used.

The mode of migration of vapor species can be described by diffusion and convective flow, which occur simultaneously under earth-based conditions. By selecting the proper conditions, either mode can dominate in the CVT process. Current theory dictates that the crystal growth rate, or mass flux, is affected by the total pressure within the reaction vessel. For example, under very low pressures, the flux is limited by heterogeneous gas/solid reactions. This is reflected in the proportionality of transport rate to transport agent pressure under these conditions. At high pressures, diffusion controls the transport rate, which is inversely proportional to total pressure in this region. At higher pressures, CVI is driven by convection, and the transport rate once again increases with increasing pressure.

Crystal morphology can be qualitatively related to gaseous transport modes. Numerous earth-based studies have shown that the highest degree of

crystal perfection is attained under conditions where CVT is diffusion-controlled whereas crystals grown under conditions where convective flow predominates are of poorer quality. Typical of this behavior is the growth of GeSe using GeI_4 as a transport agent. In the diffusion controlled transport regime, thin platelets are obtained. In contrast, dendritic growth of GeSe is observed under conditions where convection dominates the CVT process.

The above conditions defined the limitations of earth-based experimentation in the field of CVT. Attempts to eliminate convection through changes in orientation, such as vertical stabilizing temperature gradients, did meet with some success. Yet, as discussed previously, convection did persist to some extent. It was first anticipated that convection would not occur in the absence of gravity, leaving only the pressure ranges where heterogeneous reactions and diffusion controlled the mass transport rate. Changes in morphology and crystal perfection observed when CVT was performed in microgravity were also of interest.

Experiment M556, flown aboard Skylab, was the first CVT experiment performed in space. The chemical systems studied, GeSe-GeI_4 and GeTe-GeI_4 , were selected on the bases of furnace capability in Skylab and earth-based work done on these systems. Although the applications of these materials are limited, their properties may serve as models for systems having more direct application. Transport ampules were prepared so that data would be collected in pressure regions where the influence of convection under earth-based experiment conditions would vary from small, to moderate, to great.

Distinct differences in morphologies of earth-based and space-grown crystals were observed, especially in the pressure region where the convective contribution would be expected to be the greatest. Crystals grown in space

possessed smoother faces, more well-defined facets, and a higher degree of structural perfection. The growth rates achieved in space were surprisingly greater than those predicted by models which assume pure diffusion controlled CVT.

Experiment MA085, carried aboard the Apollo Soyuz Test Project (ASTP), broadened the scope of the Skylab experiments by using more complex CVT systems, namely solid solutions (GeSe-GeTe, GeS-GeSe) and in one experiment, additions of Ar gas, which varied the partial pressure of the transport agent independently of the total ampule pressure. As in the Skylab study, crystals grown in microgravity exhibited a higher degree of perfection as evidenced by the homogeneous distribution of dopants throughout the crystals, smoother facets, and well-defined edges. Growth rates were once again greater than predicted values, which at the time were attributed to thermochemical effects of gas phase reactions.

In the interim between the ASTP flight and the onset of the Space Shuttle program, earth-based experiments were carried out in an attempt to better understand the results obtained in space. These studies included effects of reaction vessel orientation upon transport rates and local temperature variations. Another CVT experiment was flown on the Shuttle in 1983. The results once again demonstrated that crystals of much higher quality can be grown in a microgravity environment.

III. Future of Crystal Growth in Space

Before discussing the future of crystal growth in space, the direction of the space program should be briefly mentioned. Emphasis is currently being placed upon a permanent American presence in space in the form of a space station in LEO. One of the missions of a space station is that of zero-

gravity materials processing on a small industrial scale, that is, passing from exploratory experiments to the manufacture of materials of practical use. The activity would first be at a level where process feasibility is demonstrated, to be followed later by actual production. A lunar base, planned for the early 21st century, would also involve some manufacturing.

The CVT technique which has been described has demonstrated the utility of microgravity processing of semiconductor materials and the advantages of growth of crystals from the vapor in this environment. Yet, CVT is not a viable means of manufacturing such materials for several reasons. First, it does not necessarily provide industrially acceptable materials. Although some exploratory work has been done in the growth of epitaxial layers by CVT, numerous single crystals of various sizes and shapes are usually obtained by this method. For application purposes, it is advantageous to grow crystalline materials directly onto a substrate. Second, because of random nucleation and size distribution, the number of usable crystals produced by CVT on a per unit basis is very small. Third, the experimental conditions such as transport agent pressure, amount of source material, and temperature gradient are not easily altered.

Many features of CVT are shared by other techniques used for growing crystals from the vapor. Gaseous flow plays an important role in different types of vapor phase epitaxy techniques, and convection presumably has a similar effect upon crystal morphology in an open chemical vapor deposition (CVD) system as in a closed CVT system. The quality of crystalline layers grown by CVD could therefore be improved if the process were carried out in microgravity. The advantage in such a technique over chemical transport is that useful materials can be directly deposited onto appropriate substrates.

Conditions which govern growth rates can be more easily altered, and the amount of materials grown per reactor is considerably larger than that afforded by CVT. In short, the introduction of this type of crystal growth into space would take materials processing in microgravity from the purely experimental stage to the level of manufacturing useful materials which are superior to their earth-based counterparts.

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